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14. ABSTRACT Various aspects of plasmonic catalysis, including plasmon enhanced catalysis, plasmonic sensing of catalysis and surface plasmon driven hot electron flow were explored. Light trapping from nanostructured Au nanopillars and their surface plasmon enhanced the photocurrent of an iron oxide photoanode by more than 50% across the solar spectrum. Two platforms for <i>in situ</i> plasmon enhanced spectroscopy of catalytic intermediates were demonstrated. Firstly, single particle hydrogen storage trajectories were monitored by recording the scattering associated with the localized surface plasmon resonance (LSPR) of Au antennas. Shape dependent hydrogen storage trajectories of Pd nanoparticles that would be lost by ensemble averaging were observed. Secondly, new Ag-alumina hybrid platforms for reproducible surface enhanced raman spectroscopy (SERS) measurements were fabricated. The photooxidation of water on titania was shown to occur by nucleophilic attack. These plasmon enhanced sensing schemes enable catalytic intermediates that are spectroscopically silent or weak to be monitored.					
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Comprehensive summary of significant work:

- Researchers followed the trajectories of hydrogen storage in single Pd nanoparticles using Au as a plasmonic probe, with direct and indirect sensing schemes. Hydrogen absorption and desorption trajectories from individual particles were disentangled from ensemble averaging.
- In indirect sensing scheme, a Pd dot is patterned in the near-field of an Au antenna with great precision. Geometric enhancement of the electromagnetic field with triangular Au antennas results in a larger sensing response compared to Au rod antennas.
- Au/Pd core/shell nanoparticles for the direct sensing experiment yielded larger LSPR shifts as both materials were in contact. Notably, shape dependent hydrogen uptake trajectories were observed. The majority of these core-shell particles displayed red and blue LSPR shifts with increasing and decreasing partial pressures of hydrogen respectively, as hydrogen intercalated reversibly into palladium. However, 20% of the particles, mainly those with thicker Pd shells, showed LSPR shifts that cannot be merely explained by hydride formation. These unexpected LSPR shifts may be explained by Au/Pd interdiffusion or silicide formation.
- This non-invasive, in situ sensing platform underlies the need for more single particle studies of catalytically active nanoparticles. This work shows that single particle techniques are vital in retaining information that would be lost in ensemble averaging.
- Hot electron flow generated on a gold thin film by photon absorption (or internal photoemission) was amplified by localized surface plasmon resonance.
- Direct measurement of photocurrent on a chemically modified gold thin film of metal-semiconductor (TiO_2) Schottky diodes.
- Intrinsic correlation between the hot electron flow generated by internal photoemission and localized surface plasmon.
- This project demonstrated enhanced photocurrent in a thin-film iron oxide photoanode coated on arrays of Au nanopillars. A net enhancement as high as 50% was observed over the solar spectrum. The enhancement can be attributed primarily to the increased optical absorption originating from both surface plasmon resonances and photonic-mode light trapping in the nanostructured topography.
- Project demonstrated a new type of Ag-alumina hybrid SERS platforms for detection of surface reaction spectroscopically in real time. The reaction intermediates of water oxidation on TiO_2 surface were observed in real time under UV irradiation. Surface intermediate bands, which correspond to peroxy, hydroperoxy and hydroxyl of titania surface intermediate species were clearly observed, suggesting that the photooxidation of water splitting was initiated by nucleophilic attack mechanism.

Catalytically active nanoparticles were interrogated at the single particle level using a plasmonic sensing scheme. The activity and selectivity of heterogeneous catalysts is uniquely dependent on their size, shape, faceting and support. Heterogeneous catalyst particles also tend to evolve as the reaction proceeds. Single particle studies of catalytically active nanoparticles deconvolute the trajectory of individual particles, retaining information that would be lost by ensemble averaging. Hydrogen storage was chosen as a model reaction to study catalyst nanoparticles at the single particle level. As hydrogen gas dissociates and intercalates into Pd, Pd changes from a metal to a semi-metal. This change in the dielectric function of Pd gives rise to a change in the refractive index in the near-field of the Au antenna, shifting its localized surface plasmon resonance (LSPR). More oblate particles show a larger sensing response due to field enhancement. Shape dependent hydrogen storage trajectories are observed for Au/Pd core/shell nanocrystals.

Our second plasmon enhanced sensing scheme of catalytically active intermediates involved a new type of Ag-alumina hybrid SERS platform for spectroscopy of surface reactions in real time. Langmuir-Blodgett technique was employed as a large scale assembly technique to self-assemble faceted Ag nanocrystals into monolayers of sensor arrays with reproducible SERS signals. The Ag nanostructures platforms were then coated with a thin layer of alumina by atomic layer deposition to prevent charge transfer between photocatalyst and Ag during photocatalysis. A single layer of ~ 5 nm thick Pt co-catalyst coated anatase TiO_2 nanocrystals with predominantly {001} facets were subsequently assembled onto the SERS platforms by Langmuir-Blodgett technique. The surface-enhanced Raman vibrations of distorted surface Ti-O-Ti bands and reaction intermediates of water oxidation on TiO_2 surface were observed in real time under UV irradiation. Surface intermediate bands, which correspond to peroxy, hydroperoxy and hydroxyl of titania surface intermediate species were clearly observed. The detection of titania peroxy and hydroperoxy species suggested the photooxidation of water splitting was initiated by nucleophilic attack mechanism.

In summary, researchers developed two plasmon enhanced sensing platforms for the in situ detection of intermediates in catalysis. They also examined the plasmonic enhancement of iron oxide photoanodes, and the amplification of hot electrons by the localized surface plasmon resonance of gold. This body of work illuminated spectroscopically silent or weak intermediates, and thus contributed directly to the rational design of catalysts.

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